SPECIFIC HEAT OF A CLASSICAL MONATOMIC IMPERFECT GAS TRAPPED IN THE SUTHERLAND POTENTIAL

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ABSTRACT

An imperfect monatomic gas of volume V and temperature T is trapped in the Sutherland potential. In this communication, we study the thermodynamic properties, in particular, the specific heat at constant volume of this imperfect gas in the classical approximation at least qualitatively and present our results.

INTRODUCTION

We consider a monatomic classical gas of N interacting particles in a volume V at an absolute temperature T. In this paper, we'll determine the first order corrections to various thermodynamic parameters. We will concentrate particularly on the specific heat at constant volume for this imperfect gas by employing the very popular Sutherland potential, namely

$$\begin{aligned} u(r) &\to \infty \qquad \text{for } r < r_0 \\ &= -\varepsilon\left(\frac{\sigma}{r}\right)^6 \quad \text{for } r > r_0 \end{aligned} \tag{1}$$

Before proceeding to study the thermodynamic properties of the gas, we first try to justify the choice of this type of potential in our problem. We note that the most significant features of an actual inter-particle potential are well described by the Lennard-Jones formula, namely

$$u(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right] \tag{2}$$

The function $u(r)$ given by the above equation shows a 'minimum' of value $-\varepsilon$ at a distance $r_0\left(= 2^{1/6}\sigma\right)$ and rises to an infinitely large (positive) value for $r < \sigma$ and to a vanishingly small (negative) value for $r \geq \sigma$. For most practical purposes, the repulsive part of the potential is not very important. It may be approximately replaced by

$$u(r) = +\infty \qquad (\text{ for } r < r_0 \text{ }) \tag{3}$$

which amounts to attributing an impenetrable core of diameter r_0 to each particle. The precise form of the attractive part is, however, important. In view of the fact that there exits good theoretical basis for the sixth-power attracting potential, this part may simply be written as

$$u(r) = -u_0\left(\frac{r_0}{r}\right)^6 \qquad (\text{ for } r \geq r_0 \text{ }) \tag{4}$$

Therefore, the potential given by Eqs. (3) and (4) may be used , if one is only interested in a qualitative assessment of the situation and not in a quantitative comparison between theory and experiment. Hence the justification of the choice of the Sutherland potential [Eq.(1)].

Now, the total energy of the system is simply the algebraic sum of the total kinetic energy and the potential energy U. Since the gas is assumed to be monatomic, the total kinetic energy is the sum of the translational energies of the N molecules. Hence, the total energy of the system can be written as

$$E = \sum_{i=1}^{N} \frac{p_i^2}{2m} + U(\vec{r_1}, \vec{r_2} \ldots \ldots \vec{r_N}, \vec{p_1}, \vec{p_2} \ldots \ldots \vec{p_N}) \tag{5}$$

where $\vec{r_i}$ and $\vec{p_i}$ are respectively the position and momentum coordinates of the ith molecule and m, the mass of a molecule. For the sake of simplicity, we assume that the interaction potential is independent of the momentum coordinates and particles interact pair-wise. The interaction between any pair of the particles (i, j) depends only on $r_{ij} = |\vec{r_i} - \vec{r_j}|$, the magnitude of the separation vector between the ith and jth particles. Thus

$$U = \sum_{pairs} u(r_{ij}) = \sum_{pairs} u_{ij} \tag{6}$$

where we write $u(r_{ij})$ as u_{ij}.

The canonical partition function for the system is then given by

$$Z(N,V,T) = \frac{1}{N!} \iint \ldots \int \frac{d^3p_1 d^3p_2 \ldots\ldots d^3p_N d^3r_1 d^3r_2 \ldots d^3r_N}{h^{3N}} exp\left[-\beta\left(\sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{pairs} u_{ij}\right)\right]$$

$$= \frac{1}{N! h^{3N}} \iint \ldots \int d^3p_1 d^3p_2 \ldots\ldots d^3p_N \, exp\left[-\frac{\beta}{2m}(p_1^2 + p_2^2 + \cdots p_N^2)\right] \times$$

$$\iint \ldots \int d^3r_1 d^3r_2 \ldots\ldots d^3r_N \prod_{pairs} exp[-\beta u_{ij}]$$

But

$$\iint \ldots \int d^3p_1 d^3p_2 \ldots\ldots d^3p_N \, exp\left[-\frac{\beta}{2m}(p_1^2 + p_2^2 + \cdots p_N^2)\right]$$

$$= \left[\int exp\left(-\frac{\beta p^2}{2m}\right)\right]^N = (2\pi mkT)^{3N/2} \tag{7}$$

and let

$$\iint \ldots \int d^3r_1 d^3r_2 \ldots\ldots d^3r_N \prod_{pairs} exp[-\beta u_{ij}] = Q(N,V,T) \tag{8}$$

which is called the configurational partition function of the system.

$$\therefore Z(N,V,T) = \frac{1}{N!}\left[\frac{\sqrt{2\pi mkT}}{h}\right]^{3N} Q(N,V,T) = \frac{1}{N! \bar{\lambda}^{3N}} Q(N,V,T) \tag{9}$$

where

$\bar{\lambda} = \frac{h}{\sqrt{2\pi mkT}}$, the mean thermal or de Broglie wavelength.

The integrand of Eq.(8) is very difficult to deal with. To tackle this problem, we introduce the two-particle function f_{ij}, defined by

$$f_{ij} = exp(-\beta u_{ij}) - 1 \tag{10}$$

The function f_{ij} is known as Ursell-Mayer function. Substituting Eq. (10) in (8), we get

$$Q(N,V,T) = \iint \dots \int d^3r_1 d^3r_2 \dots\dots d^3r_N \prod_{pairs}(1+f_{ij})$$

$$= \iint \dots \int [1 + (f_{12} + f_{13} + \cdots) + (f_{12}f_{13} + f_{12}f_{23} + \cdots) + f_{12}f_{23}f_{31} + ..] \, d^3r_1 d^3r_2 \dots\dots d^3r_N$$

We now recall that the configuration partition function $Q(N,V,T)$ is determined by the method of cluster expansion and it is very inconvenient to work with the canonical partition function $Z(N,V,T)$, because of the imposed restriction. So, we switch over to the grand canonical ensemble, where such restriction disappears. Without going to mathematical details, the grand canonical partition function is given by

$$Z(\mu,V,T) = \prod_{l=1}^{N} exp\left[\frac{Vb_l z^l}{\lambda^3}\right] \Rightarrow lnZ = \frac{V}{\lambda^3}\sum_{l=1}^{N} b_l z^l \quad (11)$$

where μ is the chemical potential and $z\left(= e^{\mu\beta}\right)$ is known as fugacity. b_l is the l-cluster integral, related to the virial coefficients a_l:

$a_1 = b_1 = 1$
$a_2 = -b_2$
$a_3 = 4b_2^2 - 2b_3$ (12)
and so on.

Thus the first virial coefficient $a_1 = b_1 = 1$ and the other virial coefficients can be determined by evaluating the cluster integrals. The second virial coefficient a_2 can be obtained from the two particle connected integral and is given by

$$a_2 = -b_2 = -\frac{1}{2V\lambda^3}\iint d^3r_1 d^3r_2 f_{12} = -\frac{1}{2V\lambda^3}\iint d^3r_1 d^3r_2 f(|\vec{r_1} - \vec{r_2}|)$$

Let $\vec{r} = \vec{r_1} - \vec{r_2}$ and $\vec{R} = \frac{(\vec{r_1}+\vec{r_2})}{2}$. Then the transformation Jacobian is

$$J = \begin{vmatrix} \frac{\partial\vec{r_1}}{\partial\vec{R}} & \frac{\partial\vec{r_2}}{\partial\vec{R}} \\ \frac{\partial\vec{r_1}}{\partial\vec{r}} & \frac{\partial\vec{r_2}}{\partial\vec{r}} \end{vmatrix} = \begin{vmatrix} 1 & 1 \\ \frac{1}{2} & -\frac{1}{2} \end{vmatrix} = -1 \Rightarrow |J| = 1 \Rightarrow d^3r_1 d^3r_2 = d^3r d^3R$$

$$\therefore a_2 = -b_2 = -\frac{1}{2V\lambda^3}\iint d^3r d^3R f(r) = -\frac{2\pi}{\lambda^3}\int_0^\infty r^2 f(r) dr$$
$$= -\frac{2\pi}{\lambda^3}\int_0^\infty r^2[exp\{-\beta u(r)\} - 1]dr \quad (13)$$

Once we know the potential $u(r)$, we can evaluate b_2 and hence a_2. In our case, the function $u(r)$ is given by Eq.(1). With this potential function, the second virial coefficient is found to be

$$a_2 = -b_2 = -\frac{2\pi}{\lambda^3}\left[\int_0^{r_0} r^2[exp\{-\beta \times \infty\} - 1]\, dr + \int_{r_0}^\infty r^2\left[exp\left\{\beta\varepsilon\left(\frac{\sigma}{r}\right)^6\right\} - 1\right] dr\right]$$

$$= -\frac{2\pi}{\lambda^3}\left[-\int_0^{r_0} r^2 dr + \int_{r_0}^\infty r^2\left[exp\left\{\beta\varepsilon\left(\frac{\sigma}{r}\right)^6\right\} - 1\right] dr\right] \quad (14)$$

We now assume that $\beta\epsilon\left(= \frac{\varepsilon}{kT}\right) \ll 1$ and so

$$a_2 = -b_2 = \frac{2\pi r_0^3}{3\bar{\bar{\lambda}}^3}\left[1 - \frac{\varepsilon}{kT}\left(\frac{\sigma}{r_0}\right)^6\right] = \frac{1}{2}\frac{\frac{4}{3}\pi r_0^3}{\bar{\bar{\lambda}}^3}\left[1 - \frac{\varepsilon}{kT}\left(\frac{\sigma}{r_0}\right)^6\right] \tag{15}$$

Let us now revert back to the main focus we promised to address namely the study of thermodynamic properties of the monatomic real gas. Using Eq.(11), the internal energy of the system is given by

$$E_{int} = -\left(\frac{\partial lnZ}{\partial \beta}\right)_{z,V} = kT^2\left(\frac{\partial lnZ}{\partial T}\right)_{z,V} = \frac{3}{2}kTV\frac{1}{\bar{\bar{\lambda}}^3}\sum_{l=1}^{N} b_l z^l \tag{16}$$

and the thermodynamic pressure is

$$P = kT\frac{1}{\bar{\bar{\lambda}}^3}\sum_{l=1}^{N} b_l z^l \tag{17}$$

From Eqs. (16) and (17)

$$P = \frac{2}{3}\left(\frac{E_{int}}{V}\right) \tag{18}$$

The specific heat at constant volume is given by

$$C_V = \left(\frac{\partial E_{int}}{\partial T}\right)_{N,V} = \frac{3}{2}Nk\left[\frac{\partial}{\partial T}\left(\frac{PV}{Nk}\right)\right]_{N,V} \tag{19}$$

Now the virial expansion of the equation of state is

$$\frac{PV}{NkT} = \sum_{l=0}^{\infty} a_l\left(\frac{\bar{\bar{\lambda}}}{v}\right)^{l-1} \quad (\text{where } v = \frac{V}{N}) \tag{20}$$

$$\Rightarrow \left[\frac{\partial}{\partial T}\left(\frac{PV}{Nk}\right)\right]_{N,V} = \sum_{l=0}^{\infty}\left(\frac{5-3l}{2}\right) a_l\left(\frac{\bar{\bar{\lambda}}^3}{v}\right)^{l-1} \tag{21}$$

From Eqs.(19) and (21)

$$C_V = \frac{3}{2}Nk\sum_{l=0}^{\infty}\left(\frac{5-3l}{2}\right) a_l\left(\frac{\bar{\bar{\lambda}}^3}{v}\right)^{l-1} = \frac{3}{2}Nk\left[a_1 - \frac{1}{2}a_2\left(\frac{\bar{\bar{\lambda}}^3}{v}\right) - \cdots\right] \tag{22}$$

Using Eqs.(12) and (15) in (22), we finally get

$$C_V = \frac{3}{2}Nk\left[1 + \frac{1}{4}\left(\frac{\frac{4}{3}\pi r_0^3}{v}\right)\left(\frac{\sigma}{r_0}\right)^6\frac{\varepsilon}{kT} + \cdots\right] \tag{23}$$

This is the result that we wanted to make.

We end up with the conclusion that in the above derivation, it was explicitly assumed that the potential $u(r)$ is given by the simplified expressions Eq.(1) and $\frac{\varepsilon}{kT} \ll 1$. So the formula Eq.(15) is not a faithful representation of the second virial coefficient of a real gas. A better evaluation of this coefficient can be made with the use of a more realistic potential function. Also, from the above discussion, we see that the specific heat of a monatomic imperfect gas is temperature-dependent and influenced by intermolecular forces. The intermolecular forces require the energy to overcome during heating, leading to a higher specific heat compared to ideal gases. In the polyatomic case, the molecules have more degrees of freedom (rotational and vibrational), particularly at higher temperatures, so that they are able to absorb energy, resulting in a higher specific heat.

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